CO Sensors for Reformate Powered Fuel Cells

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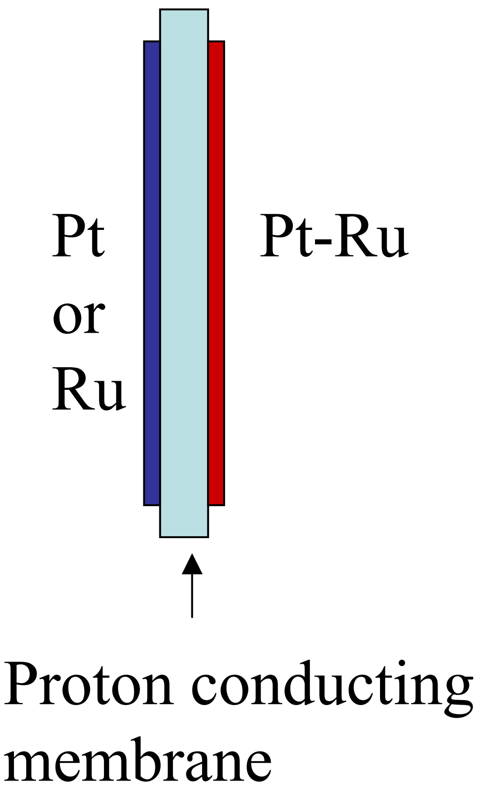
Objectives

- Reformate gas powered fuel cell systems require sensors for carbon monoxide level monitoring and feedback control
  - A high temperature sensor (>200^{o}C) is required for measurement of 0.1 to 2% CO in reformate gas for PROX reactor control
    - The reformate gas could either be from a low temperature WGS reactor or methanol reformer
  - A low temperature sensor for measuring 10-100 ppm CO concentrations for stack poisoning control
    - This sensor can be used to control the air bleed into the fuel cell anode
    - This sensor could also be used to control the oxygen input of the PROX reactor

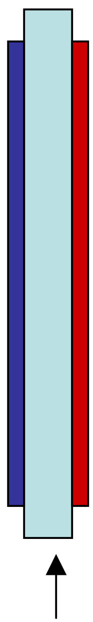
Approach (Low Temperature)

- Low temperature amperometric device based on CO inhibition of hydrogen oxidation kinetics
  - Use Nafion® as the proton conducting membrane
  - Use Pt or Ru electrode as working electrode
    - Electrode is sensitive to CO poisoning
  - Use Pt-Ru electrode as a counter electrode
    - Electrode is tolerant to the presence of CO



Approach (High Temperature)

- High Temperature device based on the differential inhibition of the hydrogen oxidation reaction at an oxide/metal interface
  - Use high temperature proton-conducting oxides like strontium and barium cerate or calcium and strontium zirconate
    - Commercially available H_2 sensor (NOTORP, TYK America)
    - Modify electrode configurations to study CO poisoning effects



Approach (High Temperature)

- Potentiometric CO sensor based on the mixed-potential developed at an oxide electrolyte/metal electrode interface

$$V_O^{\cdot\cdot} + \tfrac{1}{2}O_2 + 2e^- \rightarrow O_O$$

CO sensor in air

$$CO + O_O \rightarrow CO_2 + V_O^{\cdot\cdot} + 2e^-$$

CO sensor in H_2

$$H_2 + O_O \rightarrow H_2O + V_O^{\cdot\cdot} + 2e^-$$

- Use YSZ(zirconia) and CGO(Ceria) electrolytes
- Use various (Pt, Pd, Au, Ni) metal electrode combinations

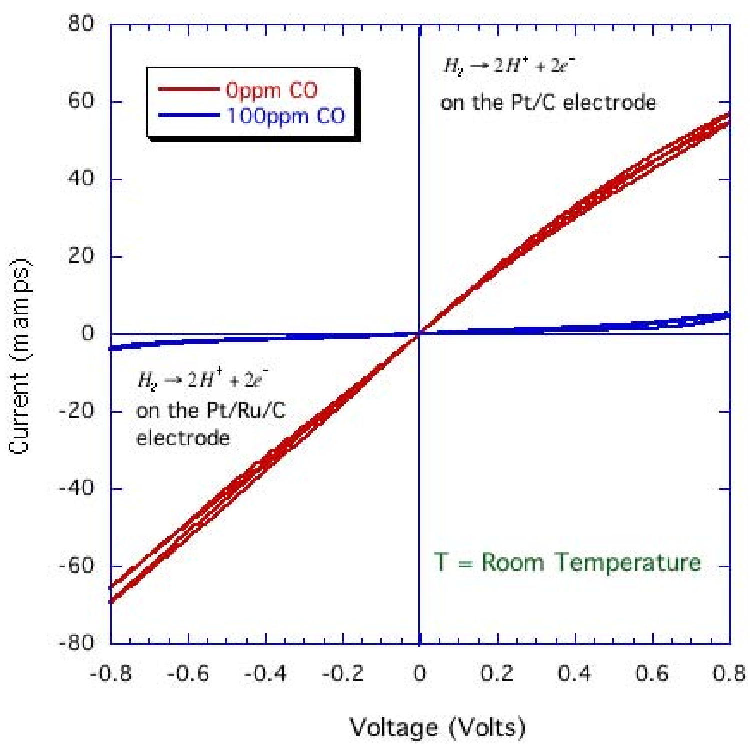
A. Hashimoto et al. *Electrochem. and Solid State Letters*, **5(1)** H1-H3 (2002)

Accomplishments (Low temperature)

- Working Electrode
  - Pt/C/Nafion : 0.22mg/cm^2 of Pt
- Counter Electrode
  - Pt/Ru/C/Nafion : 0.25mg/cm^2 of Pt/Ru(50/50)alloy
- Electrolyte
  - Nafion 1135

- Both the Pt/C and the Pt/Ru/C electrodes are good at hydrogen oxidation and both of them get poisoned by the CO

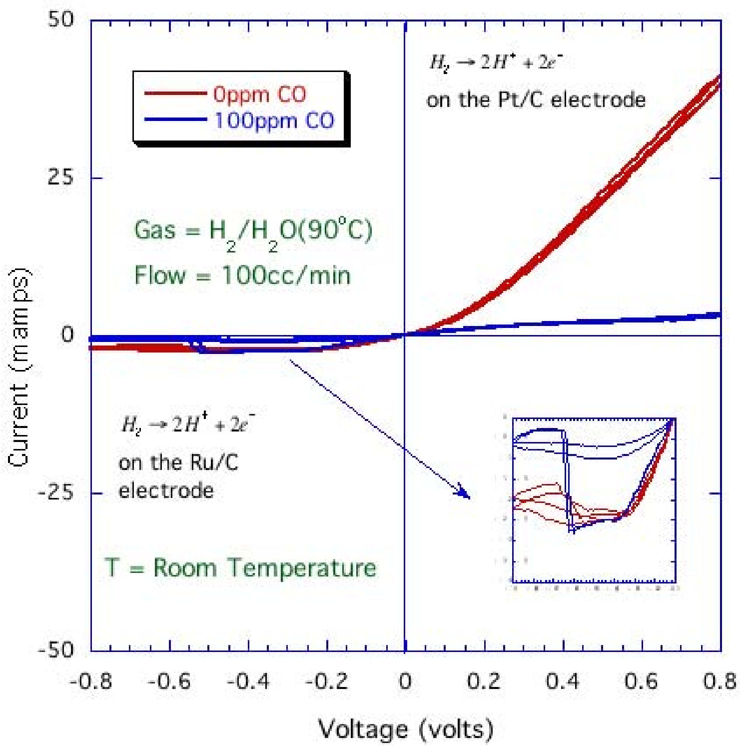
- The CO poisoning is not easily reversible
  - Recovery takes hours without air bleeding



Accomplishments (Low temperature)

- Working Electrode
  - Pt/C/Nafion : 0.22mg/cm^2 of Pt
- Counter Electrode
  - Ru/C/Nafion : 0.12mg/cm^2 of Ru
- Electrolyte
  - Nafion 1135

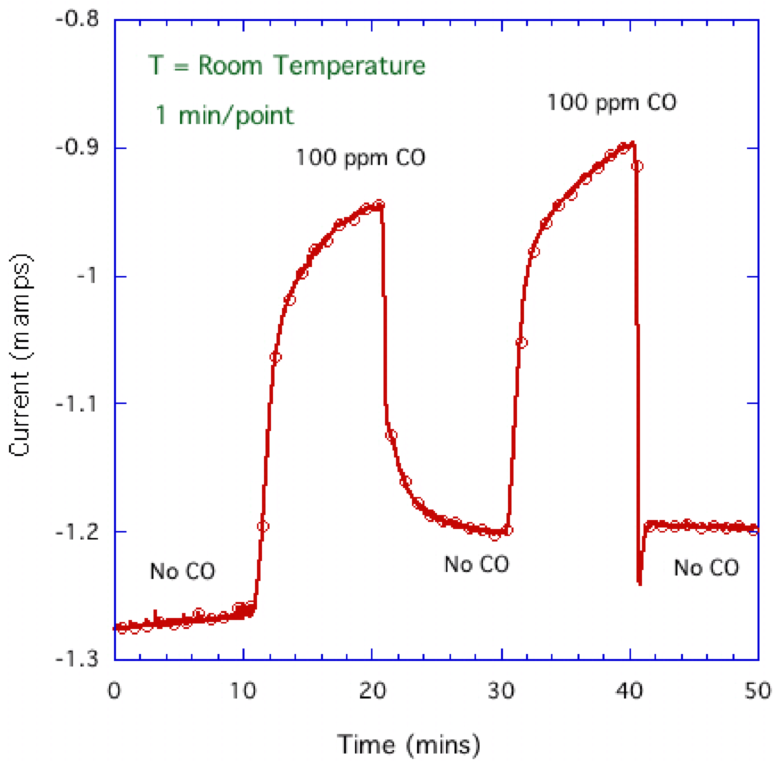
- The Ru/C electrode is not very efficient at H_2 oxidation
- Both the electrodes get poisoned by the CO, the Ru/C electrode to a lesser extent
- The CO from the Ru/C electrode can be easily stripped at voltages <-0.5V (see inset)



Accomplishments (Low temperature)

- Working Electrode
  - Pt/C/Nafion : 0.22mg/cm^2 of Pt
- Counter Electrode
  - Ru/C/Nafion : 0.12mg/cm^2 of Ru
- Electrolyte
  - Nafion 1135

- Reproducible sensor signal was attainable when sensor was operated at -0.7V
- Sensor is slow, almost 10 mins to 90% of response level
- Sensitivity is low, < 0.3mamps change for 100 ppm CO



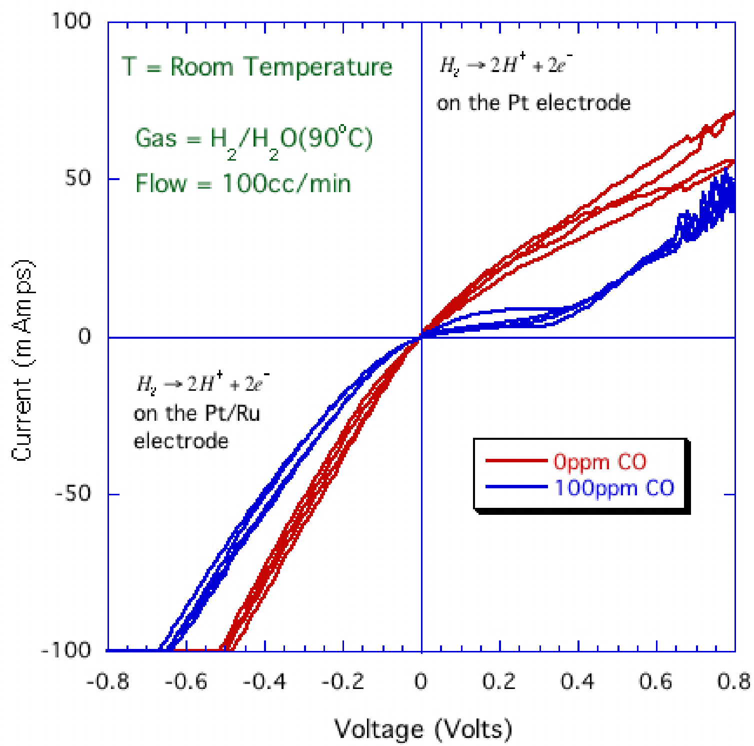
Accomplishments (Low temperature)

- Working Electrode
  - Pt/Nafion : 10mg/cm^2 of Pt
- Counter Electrode
  - Pt-Ru/Nafion : 10mg/cm^2 of Pt-Ru (50/50) alloy
- Electrolyte
  - Nafion 117

- Both the Pt and Pt/Ru alloy electrodes are good for H_2 oxidation

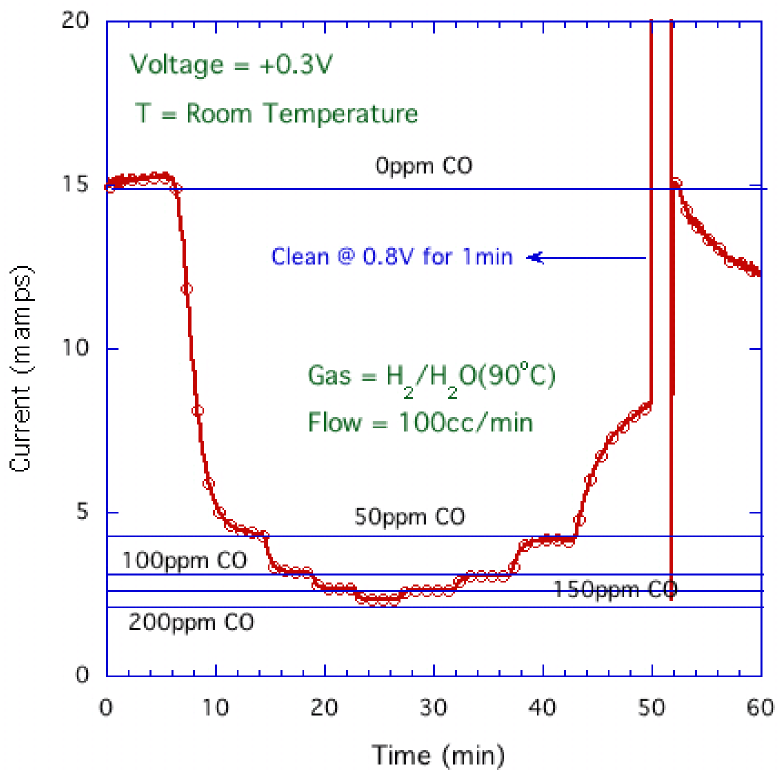
- There is very little effect of CO on the Pt/Ru alloy electrode.
  - This electrode could serve as a pseudo-reference electrode

- The Pt electrode gets poisoned by the CO which can easily be cleaned at voltages > 0.4V



Accomplishments (Low temperature)

- The extent of poisoning on the Pt electrode can be used to give a useful sensor response
- The current at 0.3V decreases from 15mamps to <5mamps when the CO content in the H_2 stream is increased from 0 to 50ppm.
- The final CO can be cleaned by applying a 0.8V potential for approx. one minute
- Slow Response time (>5 mins) when CO is introduced

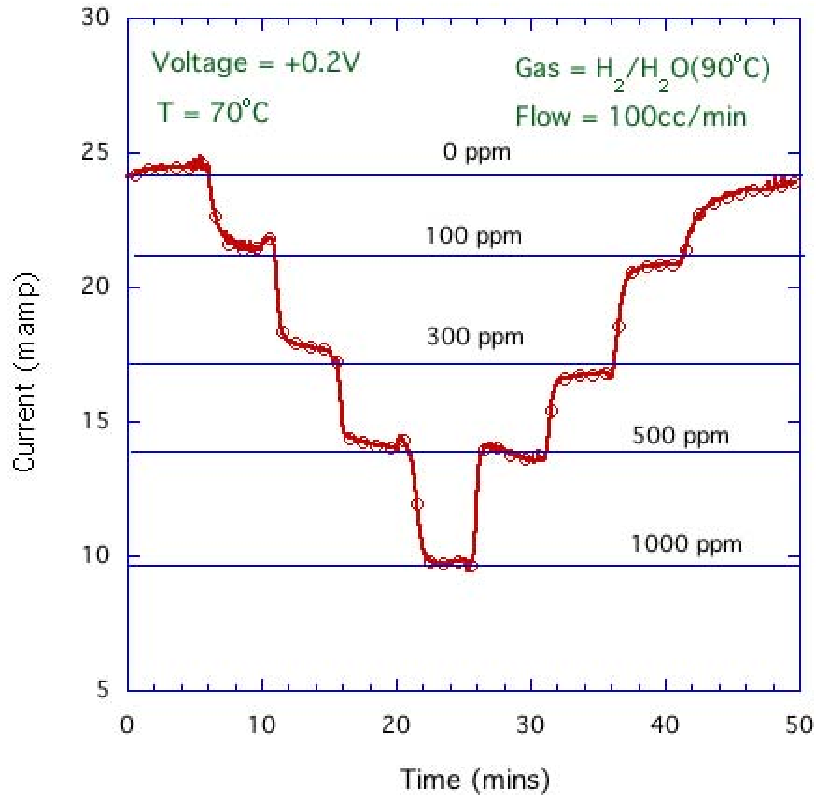


Milestone :Operation at 70^{o}C

- Stable response obtained at 70^{o}C
- Elevated temperature improves the response of the sensor
- No CO cleanup is required
- Response time : 1 - 2mins
- Sensor sensitivity is greatly reduced
    - 100 ppm of CO

      80% change at room temperature

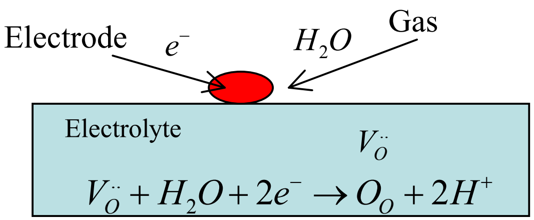
      16% change at 70^{o}C
- Baseline recovery is still slow



Useful to protect fuel cell from spikes

Proton Conductors (High Temperature)

- Electrolyte
  - $SrZr_{0.9}Y_{0.1}O_{2.95}$, $SrCe_{0.95}Yb_{0.05}O_{2.975}$ and $BaCe_{0.8}Gd_{0.2}O_{2.9}$



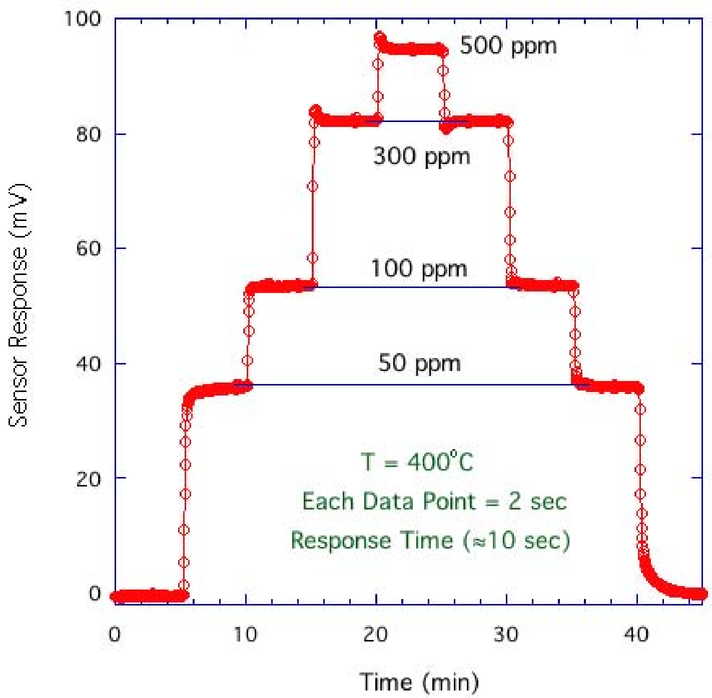
- Electrodes
  - Pt, Au, Ni and Pd
- Negligible response to CO
  - CO adsorption at temperatures >250^{o}C is not significant to affect the hydrogen oxidation reaction

$$H_2 \rightarrow 2H^+ + 2e^-$$

Oxygen Conductors (High Temperature)

- Electrolyte
  - 8mole%YSZ ($Zr_{0.85}Y_{0.15}O_{1.93}$) or 20mole%CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$) or
  - 20mole%EBO($Bi_{0.8}Er_{0.2}O_{1.9-\delta}$)
- Electrodes
  - Pt, Au
- Kinetic Control (Electrode morphology)
- Stable CO response in Air (tested for up to 2 months)
- Response time < 10sec
- Reproducible results from multiple sensors

Pt / $Ce_{0.8}Gd_{0.2}O_{1.9}$ / Au



Patent application filed

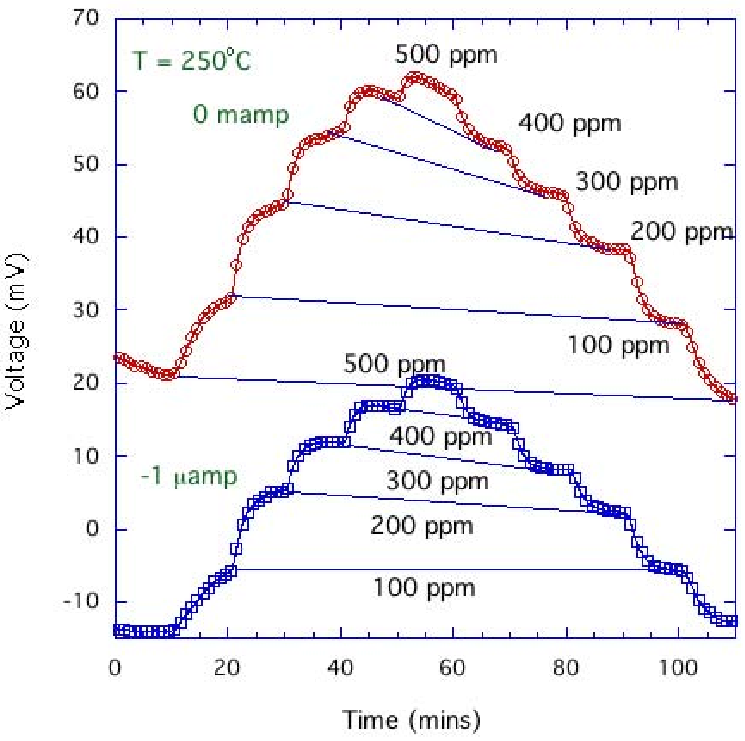
Accomplishments (High temperature)

- Electrolyte
  - 20mole%CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$)
- Electrode
  - Pt and Ni (1 μm sputtered)
- Lower operating temperature (250°C)
- Response of 35mV @ 500ppm CO
- Response decay with time
- Improvement under -ve bias

$$CO_{Ni} + O_O \rightarrow CO_2 + V_{\ddot{O}} + 2e^-$$

- The potential of the pseudo reference electrode (Ni) may be changing with time

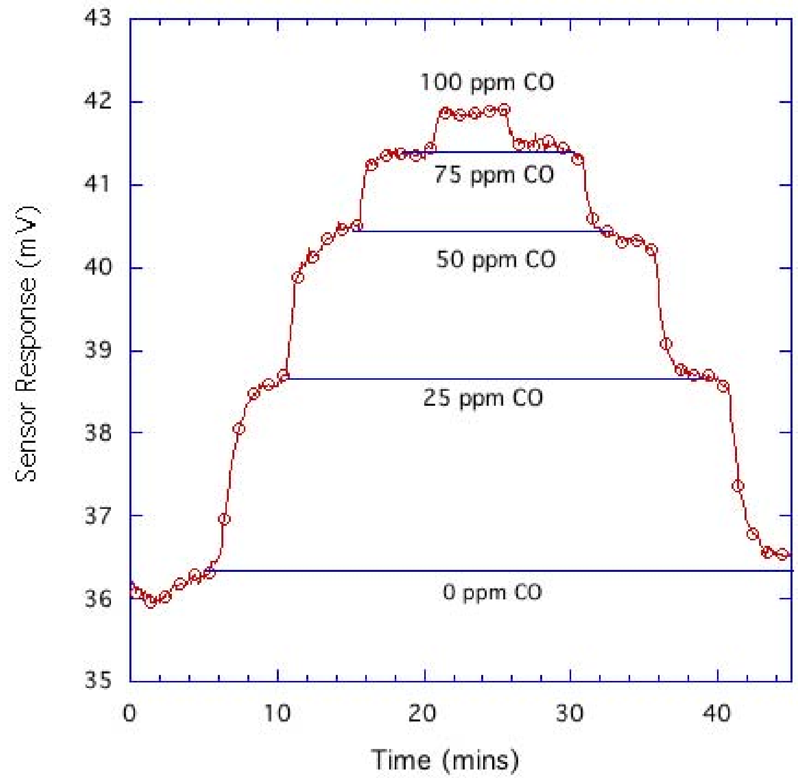
Base Gas = 70%H_2/30%CO_2(H_2O)



Milestone : Ceria based sensor

- Electrolyte
  - 20mole%CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$)
- Electrode
  - Pt and Ni (1 μm sputtered)
- Lower operating temperature (240°C)
- Response of 6mV @ 100ppm CO
- Response was stable over a period of 2 days
- Approx. 1-2 minute response time
- Unstable baseline

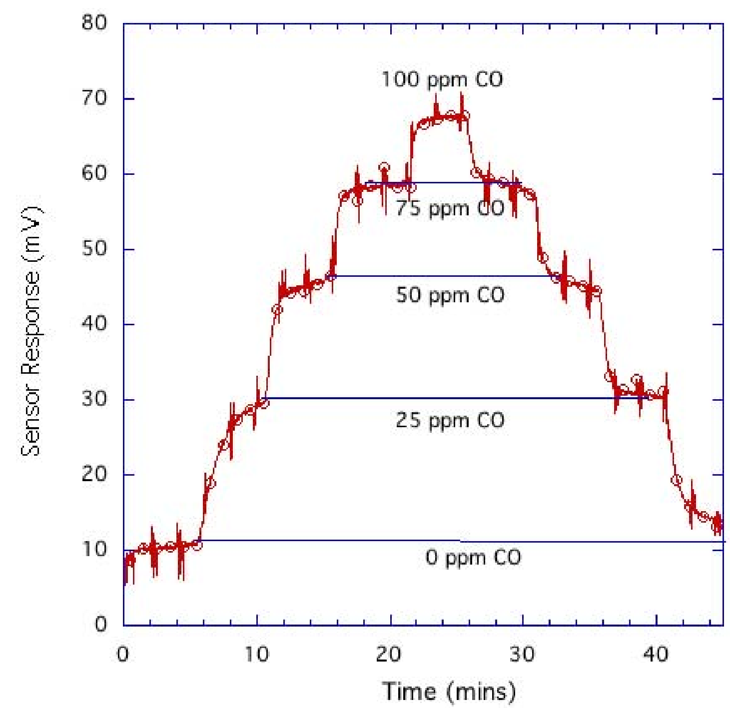
Base Gas = 70%H_2/30%CO_2(H_2O)



Improvement?

- Electrolyte
  - 3mole%YSZ
- Electrode
  - Pd paint and Ni (1 μm sputtered)
- Lowered operating temperature (185°C)
- Response of 60mV @ 100ppm CO (10 fold increase)
- Stable baseline
- Approx. 1 minute response time
- High noise (need to average)
- Stability and Reproducibility?

Base Gas = $70\%H_2/30\%CO_2(H_2O)$



Reviewer's Questions

- How is Oxygen replaced in YSZ based sensor? Stable?

$$H_2O + V_O^{\cdot\cdot} + 2e^- \rightarrow H_2 + O_O$$

  - Ceramic can operate under reformate conditions for extended periods
- Hydration, high loadings, stability of PEM assembly?
  - Novel oxide based sensor to sense 25-100ppm CO for stack control. Stable operating temperature of 200-300^{o}C should be achievable by self heated sensor positioned between PROX reactor and Fuel Cell
- <1 minute response time?
  - Demonstrated in oxide based sensor in air. Should be achievable under reformate conditions when the sensor is optimized

Project Timeline

Fy01	Fy02	Fy03	Fy04

Project begins

Low temp CO sensor prototype developed
Sense 100-1000ppm CO in H_2

Oxide proton conductor thin film technology developed

Elucidated the working principle of these low temperature sensors

Improved Low Temperature sensor
Works at Room Temperature
Stable response to 10-200ppm CO in H_2

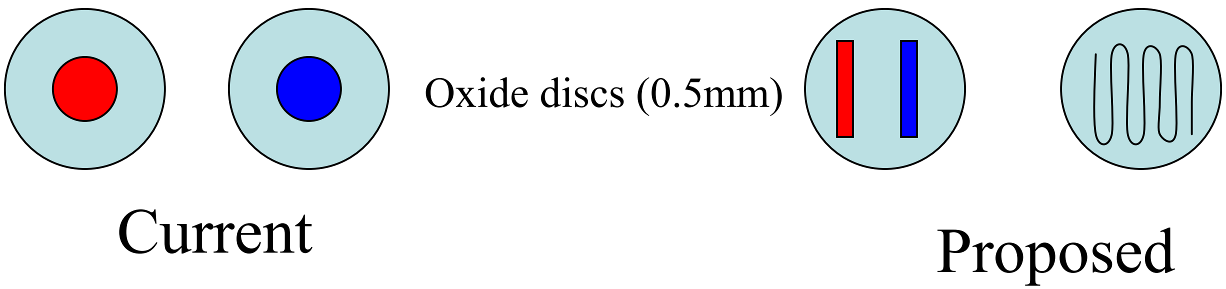
Oxide based amperometric sensors do not have sensitivity to CO and Oxide based mixed-potential sensors do not operate stabily in the presence of H_2

Demonstrate low temperature CO sensor
Stable operation at 70°C

Demonstrate higher temperature CO sensor
25-100ppm CO @ 200-300°C

Future Work (FY 04)

- Optimize Sensor : Ru and Pd sputtered electrodes
- Study response of sensors to high CO contents at 300°C
- Self heated sensor



- Test in durability test stand after PROX (Mike Inbody)

Collaborations

- Look for partners to develop CO sensor

- Worked with USCAR on DOE CRADA for hydrocarbon sensor development
- Working with ARES and University of Florida on development of NO_X sensor

Conclusions

- PEM based CO sensor has stable reproducible response to 50-200ppm of CO at room temperature
- Elevated temperatures decrease the sensitivity of the sensor while improving response time (Useful sensor to protect fuel cell from excessive CO)
- Oxide based sensors can be used to measure 25-100ppm CO in $H_2/CO_2/H_2O$ mixtures
- Stability and response time need improvement
- Oxide based sensors could be used for air(oxygen) injection control of both PROX reactor and fuel cell stack

Acknowledgements

- Bryan Pivovar and Piotr Zelenay for help with unsupported MEAs with high catalyst loadings
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